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(21) International Application Number: PCT/US98/07208 (22) International Filing Date: 13 April 1998 (13.04.98) (30) Priority Data: 08/839,047 23 April 1997 (23.04.97) US (71) Applicant (for all designated States except US): CEREL (CERAMIC TECHNOLOGIES) LTD. [IL/IL]; Science Park Technion, P.O. Box 212, 36601 Nesher (IL). (71) Applicant (for TJ only): FRIEDMAN, Mark, M. [US/IL]; Alhairs 1, 43406 Raanana (IL). (72) Inventors; and (75) Inventors/Applicants (for US only): GAL-OR, Leah [IL/IL]; Sheerith Hapleita 1, 34987 Haifa (IL). BRANDON, David [IL/IL]; Eder 16, 34752 Haifa (IL). GOLDNER, Roni [IL/IL]; Adi 426, 17940 Mizpe Adi (IL). CHERNIAK, Liudmilla [IL/IL]; Bilou 22/6, 33176 Haifa (IL). PERLIN, Leonid [IL/IL]; Abba Silver 16/24, 32694 Haifa (IL). SEZIN, Nina [IL/IL]; Ben-Yehuda 7/1, 33064 Haifa (IL). LIUBOVICH, Sonia [IL/IL]; Dr. Feiser 4, 32806 Haifa (IL).	(74) Common Representative: FRIEDMAN, Mark, M.; c/o Castorina, Anthony, Suite 207, 2001 Jefferson Davis Highway, Arlington, VA 22202 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.	
(54) Title: METHOD OF ELECTROPHORETIC DEPOSITION OF LAMINATED GREEN BODIES (57) Abstract <p>A method of electrophoretic deposition of a ceramic green body. A ceramic powder is optionally washed with a polar solvent such as deionized water, dried, and suspended in a polar organic solvent in a proportion of at least 20 % by weight. A positive surface charge is imposed on the suspended particles by conventional means such as ball milling or ultrasonic treatment. A green body is deposited on a cathode by passing a direct electric current of constant current density through the suspension. The density of the green body generally is at least 70 % of theoretical. The density of the fired body generally is at least 98 % of theoretical. A layered green body may be deposited by using several suspensions of differing global ceramic composition and depositing each microlayer in a different suspension.</p>		

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METHOD OF ELECTROPHORETIC DEPOSITION OF LAMINATED GREEN BODIES

5 FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to electrophoretic deposition and, more particularly, to a method for the electrophoretic deposition of monolithic and laminated green bodies.

10 Precisely shaped, small ceramic bodies are used in many applications, including as pitch bonding capillaries in microelectronics, as high temperature nozzles, as ferrules for connecting optical fibers, as high temperature engine components, as dental crowns and as bearing parts. To achieve the precise shaping required for the first application, bonding capillaries, it has been necessary to use the process of cold pressing to fabricate ceramic capillaries.

15 Multilayer ceramic laminates, made of sequential layers of ceramics such as alumina and zirconia, are known in a variety of geometric shapes, including plates and discs. Applications of ceramic laminates include mechanical seals, automotive engine parts, furnace elements, multilayer and FGM substrates for hybrid circuits, capacitors, RF filters, and microwave components. The processes used to fabricate ceramic
20 laminates include chemical vapor deposition (CVD) and physical vapor deposition (PVD), for layers less than about 1 micron in thickness; tape casting, for layers thicker than about 100 microns; and electrophoretic deposition (EPD), for layers between about 1 micron and about 100 microns in thickness, as will now be described.

Electrophoresis is a process in which charged ceramic particles suspended in a
25 liquid medium are attracted to an electrode when an electrical field is imposed on the particles. EPD is the process of depositing a body of a desired shape on an electrode, using electrophoresis. EPD has long been used to form green ceramic bodies. In particular, EPD has been used by Sarkar, Haung and Nicholson (Electrophoretic deposition and its use to synthesize $\text{Al}_2\text{O}_3/\text{YSZ}$ micro-laminate ceramic composites,
30 *Ceram. Eng. Sci. Proc.* vol. 14 pp. 707-716 (1993)) to deposit laminated composites of alumina and yttria-stabilized zirconia (YSZ).

There is thus widely recognized need for, and it would be highly advantageous to have, a method of EPD that can be used in the fabrication of small, precisely shaped ceramic bodies such as connecting ferrules, orifices and micro-tubes.

5 SUMMARY OF THE INVENTION

According to the present invention, there is provided a method for electrophoretic deposition of ceramic particles as a green body, including the steps of: (a) forming a first suspension of the ceramic particles in a first polar organic solvent, the ceramic particles constituting at least about 20% of the first suspension by weight; and (b) passing a first direct electrical current through the first suspension, using a deposition electrode.

According to the present invention, there is provided a green body formed of ceramic particles and having a green density of at least 70% of theoretical.

According to the present invention, there is provided a laminated ceramic body including alternating layers of a first composition and a second composition, the first composition having a higher proportion of alumina and a lower proportion of zirconia than the second composition, each of the layers of the first composition having a thickness between about 20 microns and about 40 microns, and each of the layers of the second composition having a thickness between about 30 microns and about 50 microns.

In the formation of ceramic green bodies by EPD, the ceramic particles may be positively charged, in which case they are deposited on the cathode; or they may be negatively charged, in which case they are deposited on the anode. The electrode on which the ceramic particles are deposited is referred to herein as the "deposition electrode". In the examples given herein, the deposition electrode is the cathode, but it will be understood that the scope of the present invention includes the deposition by EPD of negatively charged ceramic particles, so that the deposition electrode is the anode. A small ceramic article such as a bonding capillary or a micro-tube is formed by deposition on a deposition electrode having an external shape identical to the desired internal shape of the capillary. The green body must be sufficiently dense and rigid to retain its shape as it is removed from the deposition electrode and prepared for

sintering. To achieve the necessary mechanical strength, the green body may be deposited on the deposition electrode in microlayers, as taught by Sarkar, Haung and Nicholson. This alone, however, is insufficient to give the green body the required rigidity.

5 Sarkar, Haung and Nicholson used suspensions that included up to 10% by weight of ceramic in polar organic liquids such as ethanol, and obtained green bodies with densities of about 60% of theoretical. Surprisingly, it has been found that using denser suspensions, including from about 20% to about 70% by weight of ceramic, allows the deposition by EPD of both laminated and monolithic green bodies, with
10 densities of 70% and higher of theoretical, that retain their shape when removed from the deposition electrode and sintered. To achieve this green body density in a monolithic green body, it is necessary first to wash the ceramic powders repeatedly in a polar solvent such as deionized water, until the conductivity of the used washing solvent is essentially the same as the original conductivity of the washing solvent.
15 The utility of this washing step in the production of denser monolithic green bodies is believed to be related to the consequent reduction in the ionic conductivity of the suspension. This washing step is optional in the case of laminated green bodies. Preferably, the washed powders are dried before being added to the polar organic solvent to form the suspension.

20 Suspensions and slurries with higher concentrations of ceramic particles have been used to form green bodies by tape casting. For example, Chartier, Merle and Besson (Laminar ceramic composites, *J. Eur. Ceram. Soc.* Vol. 15 pp. 101-107 (1995)) used a slurry of greater than 60% ceramic in an azeotropic mixture of methyl ethyl ketone and ethanol to form alumina-zirconia laminates by tape casting. Tape
25 casting is not suitable for fabricating the ceramic bodies of the present application, because, as noted above, tape casting is restricted in practice to layers thicker than about 100 microns, and to flat geometries. Kerkar et al., in US Patent No. 5,194,129, teach the manufacture of optical ferrules by EPD, using *aqueous* suspensions of ceramic particles that contained about 40% to 50% by weight of ceramic. Aqueous
30 suspensions are not suitable for the present application because they are subject to electrolysis, leading to the formation of hydrogen bubbles at the cathode and a

consequent decrease in the density and local uniformity of a green body deposited thereon.

A laminated green body is formed by EPD by using two or more suspensions of differing global compositions, and alternately placing the electrodes in each of the suspensions, until the desired number of microlayers is deposited. By "global composition" is meant the composition of the ceramic component of the suspension taken as a whole. For example, a suspension of 80% Al_2O_3 and 20% ZrO_2 has a different global composition than a suspension of 40% Al_2O_3 and 60% ZrO_2 , even though the individual Al_2O_3 and ZrO_2 particles of the two suspensions are identical in composition. The microlayers are deposited at a constant current density, as taught by Sarkar, Haung and Nicholson, in order to achieve a constant rate of deposition.

The method of the present invention confers the following advantages on the resulting ceramic bodies:

- Precisely controlled shape
- Uniform and parallel layers in laminates
- High strength and toughness, in the case of multilayer laminates
- Fine, stress-free microstructure
- Near net shaped products

In addition, the method is more cost effective and less wasteful of raw materials than other methods known in the art, is environment-friendly and can be automated in a straightforward manner.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of a method of electrophoretic deposition that can be used to form green bodies of precisely controlled shapes. Specifically, the present invention can be used in the fabrication of pitch bonding capillaries.

The principles and operation of electrophoretic deposition according to the present invention may be better understood with reference to the following description.

The scope of the present invention includes particles of all suitable ceramics, both oxides and non-oxides. Non-limitative examples of suitable ceramics include

alumina, zirconia (including YSZ, CESZ and BASZ), titania, baria and mixtures thereof, such as zirconia-toughened alumina and alumina-toughened zirconia. The particles should be small enough (less than about 1 micron across) to produce a uniform deposit on the cathode.

5 The preferred polar organic solvents are pure ethanol, pure methyl ethyl ketone and mixtures of ethanol and methyl ethyl ketone in ratios of between 50:50 and 80:20. The most preferred solvent is the 60:40 azeotrope of ethanol and methyl ethyl ketone.

10 To impose the needed positive surface charge on the ceramic particles, the suspension is ball milled, using ceramic grinding media, for up to 24 hours, or subjected to 20 KHz ultrasound at a power level of up to about 550 watts, for between about 2 minutes and about 15 minutes. Optionally, additives such as pH adjustment agents, dispersants and binders are added to the suspension. The pH adjustment agent can be any suitable organic or inorganic acid that is miscible in the polar organic
15 solvent. The preferred pH adjustment agents are hydrochloric acid and acetic acid. The preferred dispersants are acetylacetone and chloroacetic acid, which have been found to allow the deposition, in laminated green bodies, of relatively smooth ceramic microlayers as thick as about 100 microns, in contrast to the prior art microlayer thicknesses of no more than about 20 microns. It should be noted that the preferred
20 microlayer thicknesses, to provide alumina-zirconia laminates of alternating alumina-rich and zirconia-rich layers with maximum strength and toughness, are between about 20 microns and about 40 microns, for the alumina-rich layer, and between about 30 microns and about 50 microns for the zirconia-rich layer. The preferred binders are polyvinyl butyral, nitrocellulose and shellac.

25 The principle criteria for selecting electrode materials is that they be inert under process conditions and inhibit the evolution of hydrogen gas. If the deposition electrode is a cathode, it may be either consumable or reusable. A consumable cathode is one that is destroyed during the sintering process, so that the green body need not be removed from the cathode before sintering. The preferred materials for a
30 consumable cathode are carbon and electrically conducting polymers. The preferred materials for a reusable cathode are stainless steel, nickel, aluminum, tungsten carbide

and noble metals such as platinum, palladium, silver and gold, and their alloys. The preferred materials for the anode are nickel and noble metals. As noted above, in the production of small ceramic articles such as micro-tubes, the cathode is a wire having a shape identical to the desired interior shape of the ceramic article. Preferably, the anode surrounds the cathode.

Also as noted above, it is necessary to inhibit the production of hydrogen gas at the cathode. In addition to using a polar organic solvent instead of water to form the suspension, this is accomplished by including a hydrogen getter and/or a surface coating on the cathode to absorb hydrogen. Preferred hydrogen getters include palladium and platinum and their alloys. In the case of stainless steel cathodes, a surface coating of a fibrous material such as lens paper has been found effective for both absorption of hydrogen and facilitating the removal of the green body from the cathode subsequent to the deposition. Removal of the green body from the cathode also is facilitated by polishing the cathode surface before deposition.

The anode and cathode are immersed in the suspension, and a direct electrical current of constant current density, as measured at the cathode, is passed between the electrodes while the suspension is stirred. The preferred range of current densities is between about 0.1 mA/cm^2 and about 5 mA/cm^2 . As noted above, to deposit a laminated green body, several suspensions of differing global composition are used, and the electrodes are moved from one suspension to another as necessary. The deposition time in each suspension depends on the desired microlayer thickness, the current density and the suspension concentration. Typical deposition times for one microlayer range from a few seconds to a few minutes. The total deposition time for a planar laminated green body is on the order of a few hours. The total deposition time for a monolithic or laminated cylindrical body, such as a pitch bonding capillary, having a diameter of a few millimeters is on the order of one minute or less.

Following the deposition, the green body is removed from the cathode, dried in a dessicator, and sintered. Pressureless sintering in air at about 1550°C for a few hours has been found suitable for the production of stress-free alumina-zirconia laminates. The sintered ceramic body may be machined and/or polished after sintering.

Example 1: Multilayer Laminate

A first suspension was prepared by dispersing 270 grams of alumina powder (average particle size 0.4 microns) and 30 grams of zirconia powder (average particle size 0.3 microns) in 1000 ml of an azeotropic mixture of ethanol and methyl ethyl ketone. A second suspension was prepared by dispersing 160 grams of the same alumina powder and 240 grams of the same zirconia powder in 1000 ml of an azeotropic mixture of ethanol and methyl ethyl ketone.

Both suspensions were prepared using 800 ml of the ethanol - methyl ethyl ketone mixture in each, and ball milled for 24 hours, using alumina balls to mill the first suspension and zirconia balls to mill the second suspension. 200 more ml of the ethanol - methyl ethyl ketone mixture was added to each suspension, to bring the total volume of solvent up to the desired 1000 ml. Enough HCl was added to each suspension to adjust the pH of the first suspension to about 7 and the pH of the second suspension to about 6. About 0.5% by volume of acetylacetone dispersant was added to the first suspension. About 1.5% by volume of acetylacetone dispersant was added to the second suspension. About 0.1% by volume of shellac binder was added to each suspension. Each suspension now was transferred to its own electrophoretic cell.

The cathode was a stainless steel plate covered with Wattman lens paper. Each electrophoretic cell was provided with its own half-cylinder nickel anode about 40mm in radius. The cathode was placed in the first electrophoretic cell at the center of curvature of the anode, and a direct electrical current having a current density of about 0.4 mA/cm^2 was passed between the electrodes for about 45 seconds. The cathode then was removed from the first electrophoretic cell and placed in the second electrophoretic cell, at the same location as before relative to the anode, and the same 0.4 mA/cm^2 of direct electrical current was run between them. This process was repeated for 50 cycles, resulting in the deposition of 100 microlayers, each about 50 microns thick, for a total laminate thickness of about 5 millimeters. A final 50 micron alumina-rich microlayer was deposited in the first electrophoretic cell. The green body was removed from the cathode, dried in a dessicator for a few hours, and sintered in air at 1550°C for 4 hours. The green body had a density of about 70% of theoretical. The sintered body had an open porosity of between 0.2% and 0.5% by

volume. The microhardness of the alumina-rich microlayers, measured by the Vickers method, was about 2400 kg/cm². The microhardness of the zirconia-rich layers was about 2000 kg/cm². The bending strength of the sintered body was about 80 kg/mm².

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Example 2: Monolithic Capillary

45 grams of alumina (average particle size 0.4 microns to 0.5 microns) and 5 grams of zirconia (average particle size 0.3 microns) were washed repeatedly with deionized water until the conductivity of the wash water fell to about 5 microsiemens/cm. The powders were dried, and enough ethanol was added to bring
10 the total volume to 100 ml. The resulting suspension was ball milled for 4 hours. 0.025 ml of acetylacetone dispersant and 2 ml of a 5% by volume solution of shellac binder in ethanol were added. The suspension was stirred for about 15 minutes and transferred to an electrophoretic cell.

Two different cathodes were used in two different runs: a graphite wire and a
15 tungsten carbide wire having external shapes identical to the internal shape of a typical bonding capillary, tapering from a 1.2 millimeter diameter at the distal end to a 0.04 millimeter diameter at the proximal end. The cathode was a nickel cylinder about 60 mm in diameter surrounding the cathode. The electrodes were placed in the electrophoretic cell and a direct electrical current having a current density of about 1.0
20 mA/cm² was run between them for about 60 seconds, resulting in the deposition of a 1 millimeter thick deposit. The density of the deposited green bodies was about 70% of theoretical. The green body on the tungsten carbide cathode was removed, and the green bodies were sintered in air at 1550°C for about 1.5 hours, yielding alumina capillaries with densities of 99% of theoretical and microhardnesses of 2500 kg/cm².

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While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.

WHAT IS CLAIMED IS:

1. A method for electrophoretic deposition of ceramic particles, comprising the steps of:

- (a) forming a first suspension of the ceramic particles in a first polar organic solvent, the ceramic particles constituting at least about 20% of said first suspension by weight; and
- (b) passing a first direct electrical current through said first suspension, using a deposition electrode;

thereby producing a green body having a density of at least 70% of theoretical.

2. The method of claim 1, wherein said first direct electrical current has a constant current density.

3. The method of claim 1, further comprising the step of:

- (c) washing said ceramic particles in a polar solvent, prior to said forming of said first suspension.

4. The method of claim 3, wherein said polar solvent includes deionized water.

5. The method of claim 1, further comprising the steps of:

- (c) forming a second suspension of the ceramic particles in a second polar organic solvent, the ceramic particles constituting at least about 20% of said second suspension by weight, the ceramic particles of said second suspension having a different global composition than the ceramic particles of said first suspension; and
- (d) passing a second direct electrical current of constant current density through said second suspension, using said deposition electrode.

6. The method of claim 5, wherein said second direct electrical current has a constant current density.

7. The method of claim 1, wherein said deposition electrode is a cathode.

8. The method of claim 7, further comprising the step of providing said cathode with a mechanism for absorbing hydrogen.

9. The method of claim 8, wherein said mechanism for absorbing hydrogen includes palladium.

10. The method of claim 8, wherein said mechanism for absorbing hydrogen includes a fibrous surface coating on said cathode.

11. The method of claim 7, wherein said cathode is made of a material selected from the group consisting of carbon, electrically conducting polymers, stainless steel, nickel, aluminum, noble metals and tungsten carbide.

12. The method of claim 7, wherein said first direct electrical current is passed between said cathode and an anode made of a material selected from the group consisting of noble metals and nickel.

13. The method of claim 2, wherein said current density of said first direct electrical current is between about 0.1 mA/cm^2 and about 5 mA/cm^2 .

14. The method of claim 1, wherein said first polar organic solvent includes at least one alcohol.

15. The method of claim 1, wherein said first polar organic solvent includes at least one ketone.

16. The method of claim 1, further comprising the step of:
 - (c) selecting the ceramic particles from the group consisting of alumina particles, zirconia particles, yttria-stabilized zirconia particles, ceria-stabilized zirconia particles, magnesia-stabilized zirconia particles, titania particles, baria particles, mixed alumina-zirconia particles, mixed alumina-titania particles, mixed zirconia-titania particles, mixed alumina-baria particles, mixed zirconia-baria particles and mixed titania-baria particles.
17. The method of claim 1, further comprising the step of:
 - (c) adding a dispersant to said first suspension.
18. The method of claim 17, wherein said dispersant is selected from the group consisting of acetylacetone and chloroacetic acid.
19. A green body formed of ceramic particles and having a green density of at least 70% of theoretical.
20. The green body of claim 19, wherein said ceramic particles are selected from the group consisting of alumina particles, zirconia particles, yttria-stabilized zirconia particles, ceria-stabilized zirconia particles, magnesia-stabilized zirconia particles, titania particles, baria particles, mixed alumina-zirconia particles, mixed alumina-titania particles, mixed zirconia-titania particles, mixed alumina-baria particles, mixed zirconia-baria particles and mixed titania-baria particles.
21. The green body of claim 19, formed by a process including electrophoretic deposition.
22. A laminated ceramic body comprising alternating layers of a first composition and a second composition, said first composition having a higher proportion of alumina and a lower proportion of zirconia than said second

composition, each of said layers of said first composition having a thickness between about 20 microns and about 40 microns, and each of said layers of said second composition having a thickness between about 30 microns and about 50 microns.

23. The ceramic body of claim 22, formed by a process including electrophoretic deposition.

24. A method for electrophoretic deposition of ceramic particles as a green body, comprising the steps of:

- (a) forming a first suspension of the ceramic particles in a first polar organic solvent, the ceramic particles constituting at least about 20% of said first suspension by weight;
- (b) passing a first direct electrical current through said first suspension, using a deposition electrode;
- (c) forming a second suspension of the ceramic particles in a second polar organic solvent, the ceramic particles constituting at least about 20% of said second suspension by weight, the ceramic particles of said second suspension having a different global composition than the ceramic particles of said first suspension; and
- (d) passing a second direct electrical current of constant current density through said second suspension, using said deposition electrode.

25. The method of claim 24, wherein said direct electrical currents have constant current densities.

26. The method of claim 25, wherein said current densities of said direct electrical currents are between about 0.1 mA/cm² and about 5 mA/cm².

27. The method of claim 24, further comprising the step of:

- (e) washing said ceramic particles in a polar solvent, prior to said forming of said first suspension and said second suspension.

28. The method of claim 27, wherein said polar solvent includes deionized water.

29. The method of claim 24, wherein said deposition electrode is a cathode.

30. The method of claim 29, further comprising the step of providing said cathode with a mechanism for absorbing hydrogen.

31. The method of claim 30, wherein said mechanism for absorbing hydrogen includes palladium.

32. The method of claim 30, wherein said mechanism for absorbing hydrogen includes a fibrous surface coating on said cathode.

33. The method of claim 29, wherein said cathode is made of a material selected from the group consisting of carbon, electrically conducting polymers, stainless steel, nickel, aluminum, noble metals and tungsten carbide.

34. The method of claim 29, wherein said direct electrical currents are passed between said cathode and an anode made of a material selected from the group consisting of noble metals and nickel.

35. The method of claim 24, wherein at least one of said polar organic solvents include at least one alcohol.

36. The method of claim 24, wherein at least one of said first polar organic solvents include at least one ketone.

37. The method of claim 24, further comprising the step of:
- (e) selecting the ceramic particles from the group consisting of alumina particles, zirconia particles, yttria-stabilized zirconia particles, ceria-stabilized zirconia particles, magnia-stabilized zirconia particles, titania particles, baria particles, mixed alumina-zirconia particles, mixed alumina-titania particles, mixed zirconia-titania particles, mixed alumina-baria particles, mixed zirconia-baria particles and mixed titania-baria particles.
38. The method of claim 24, further comprising the step of:
- (e) adding a dispersant to at least one of said suspensions.
39. The method of claim 38, wherein said dispersant is selected from the group consisting of acetylacetone and chloracetic acid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/07208

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C25D 13/02.

US CL : 204/484, 490, 491; 428/469, 472.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/484, 490, 491; 428/469, 472.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,002,647 A (TANABE et al.) 26 March 1991 (26-03-91), see abstract; column 3, lines 18-23 and examples 1-2.	1-2, 5-8, 11-16, 19-26, 29-30, and 33-37.
X	US 5,194,129 A (KERKAR et al.) 16 March 1993 (16-03-93), see abstract and claim 1.	8-9 and 31-32.
X	US 5,415,748 A (EMILIANI et al.) 16 May 1995 (16-05-95), see abstract; column 5, line 3 through column 6, line 11; and example 1.	1-8, 10-14, 16, 19-21.
X	US 2,707,703 A (DORST) 03 May 1955 (03-05-55), paragraph crossing cols. 7 and 8.	3-4, 17-18, 27-28 and 38-39.

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,021,376 A (NIENBURG et al.) 04 June 1991 (04-06-91), see abstract; column 2, lines 33-47 and column 3, lines 18-21.	17-18 and 38-39.